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Appendix F - First-order mass transfer coefficient estimation assuming pure advection

Consider a contaminant front advancing into the immobile region due to a hydraulic head gradient across a horizontal layer. Until the front reaches the other side, the net flux into the region is

$$F(t) = C_m U_{im} = C_m K_{im} \left(\frac{\partial h}{\partial z} \right)_{im} \tag{1}$$

where U_z is defined by Darcy's Law

$$U_{im} = K_{im} \left(\frac{\partial h}{\partial z} \right)_{im} \tag{2}$$

This mass flux also corresponds to the rate of mass accumulation in the immobile region

$$F(t) = \frac{\partial M_{im}}{\partial t} = \frac{\partial \theta_{im} C_{im} L_{im}}{\partial t} = L_{im} \theta_{im} \frac{\partial C_{im}}{\partial t} \tag{3}$$

where C_{im} is the spatially averaged concentration. Combining (1.1) and (1.3) yields

$$\begin{aligned} L_{im} \theta_{im} \frac{\partial C_{im}}{\partial t} &= C_m U_{im} \\ \frac{\partial C_{im}}{\partial t} &= \frac{C_m U_{im}}{L_{im} \theta_{im}} \end{aligned} \tag{4}$$

Assuming C_m is constant, equation (1.4) can be readily integrated as

$$C_{im} = \frac{C_m U_{im}}{L_{im} \theta_{im}} t \tag{5}$$

which is valid for

$$t < \frac{L_{im} \theta_{im}}{U_{im}} \equiv t_b \tag{6}$$

where t_b denotes the time required for the front to break-through the opposite site. The dual-media mass transfer coefficient is defined by

$$\theta_{im}\frac{\partial C_{im}}{\partial t}=\beta(C_m-C_{im}) \tag{7}$$

or through rearrangement of terms

$$\beta=\frac{\theta_{im}\dfrac{\partial C_{im}}{\partial t}}{C_m-C_{im}} \tag{8}$$

For the current situation of advection-driven mass transfer, introducing equation (5) into (1.8) produces

$$\beta=\frac{\theta_{im}\dfrac{C_m U_{im}}{L_{im}\theta_{im}}}{C_m-\dfrac{C_m U_{im}}{L_{im}\theta_{im}}t}=\frac{\theta_{im}}{\dfrac{L_{im}\theta_{im}}{U_{im}}-t}=\frac{\theta_{im}}{t_b-t} \tag{9}$$